⑲ Europäisches Patentamt
European Patent Office
Office européen des brevets

⑪ Publication number: **0 003 399**
A1

⑫ **EUROPEAN PATENT APPLICATION**

㉑ Application number: **79300058.9**

㉒ Date of filing: **15.01.79**

(51) Int. Cl.^{2}: C 07 C 53/02
C 07 C 53/08, C 07 C 53/22
C 07 C 51/20

㉚ Priority: **27.01.78 GB 332078**

㊸ Date of publication of application:
08.08.79 Bulletin 79/16

(84) Designated contracting states:
BE DE FR GB IT NL

(71) Applicant: **BP Chemicals Limited**
Britannic House Moor Lane
London, EC2Y 9BU(GB)

(72) Inventor: **Gasser, Clive Gordon**
BP Chemicals Limited
Saltend, Hedon Hull HU12 8DS(GB)

(72) Inventor: **Russell, John**
BP Chemicals Limited
Saltend, Hedon Hull HU12 8DS(GB)

(74) Representative: **Harry, John et al,**
BP TRADING LIMITED Patents & Licensing Division
Chertsey Road
Sunbury-on-Thames Middlesex TW16 7LN(GB)

---

(54) **Process for the liquid phase production of carboxylic acids containing 1-3 carbon atoms catalysed by phosphorus compounds.**

(57) C_1 to C_3 mono-carboxylic acids, including a substantial proportion of acetic acid, are produced by oxidising a paraffinic hydrocarbon feedstock with molecular oxygen at a temperature in the range 150 to 250°C and at an elevated pressure sufficient to maintain the reactants in the liquid phase in the presence as catalyst, of phosphoric acid and/or a phosphate of one or more metals of Groups I and II of the Periodic Table, in particular sodium or potassium. In an alternative embodiment of the invention a co-catalyst in the form of one or more metals of variable valency, particularly manganese, is incorporated in the reactants. The reaction products are recovered by distillation.

EP 0 003 399 A1

Croydon Printing Company Ltd

4513

0003399

PROCESS FOR THE LIQUID PHASE PRODUCTION OF C_1 TO C_3 CARBOXYLIC ACIDS

The present invention relates generally to the production of C_1 to C_3 carboxylic acids by the liquid phase oxidation of a paraffinic hydrocarbon feedstock and in particular to the addition of phosphoric acid and/or a phosphate of one or more metals of Groups I and II of the Periodic Table to such oxidations for the purpose of increasing the selectivity to acetic acid.

The liquid phase oxidation of a paraffinic hydrocarbon feedstock with molecular oxygen at elevated temperature and pressures to produce C_1 to C_3 carboxylic acids is a well known process and is described, for example, in British Patent Specification Nos 743,989; 743,990; 743,991; 767,290 and 771,992. The products produced by this process may be classified as (a) volatile non-acidic oxidation products of boiling-point up to 99°C in the presence of water, generally referred to as "low boilers" or "light ends", (b) water, (c) aliphatic mono-carboxylic acids of 1 to 3 carbon atoms and (d) higher boiling materials, including acids, otherwise known as "heavy ends".

The use of compounds of metals of variable valency as catalysts in paraffin oxidation processes for the purpose of increasing the overall selectivity to acids is described in the very early patent specifications referred to hereinbefore. In recent years it has been recognised that improving not only the overall selectivity to acids but also the relative amounts of particular acids in the oxidation product is a desirable objective. Thus it has been reported comparatively recently that the use of a cobalt catalyst containing at least one other metal selected from sodium, potassium, copper, magnesium, calcium, zinc, cadmium, barium, aluminium, tin, lead, nickel, or iron as catalyst increases the ratio of the yield of acetic acid to the yield of formic acid. Also British Patent Specification No 1,403,196 describes the use of a manganese compound in a concentration of from 1 to 50 parts per million based on the total weight of reaction mixture as catalyst in order to achieve improved selectivies to acetic acid on oxygen consumed. Furthermore British Patent Specification No 1,396,747 describes the addition of molybdenum in the +6 oxidation state to paraffin oxidations, again for the purpose of increasing the selectivity to acetic acid.

It has now been found that the selectivity to acetic acid can be increased by the addition to the oxidation reaction of phosphoric acid and/or a phosphate of one or more metals of Groups I and II of the Periodic Table.

Accordingly the present invention provides a process for the production of C_1 to C_3 mono-carboxylic acids, including a substantial proportion of acetic acid, by oxidising in a reaction zone a paraffinic hydrocarbon feedstock with molecular oxygen at a temperature in the range from 150 to 250°C and at an elevated pressure sufficient to maintain the reactants in the liquid phase characterised in that there is added to the reactants a compound comprising phosphoric acid and/or a phosphate of one or more metals of Groups I and II of the Periodic Table.

Any of the known types of apparatus in which molecular oxygen is intimately contacted with liquid feed may form the reaction zone. An example of a suitable form of apparatus is a vertical stainless steel tower containing a coaxial draught tube open at both ends thereof. In operation the tower is filled to at least the height of the top of the draught tube with liquid reactant, molecular-oxygen containing gas is introduced into the tower near the base and external to the draught tube. The mixture of gas and liquid rises until it is level with the top of the draught tube, whereupon the gas disengages from the liquid and the liquid descends through the draught tube to the base of the reactor where the cycle is repeated.

The paraffinic hydrocarbon is preferably a paraffin containing from 4 to 8, even more preferably 5 to 7, carbon atoms in the molecule or a mixture thereof. The paraffin may be a straight-chain paraffin, used either alone or in admixture with branched-chain and cyclic paraffins. Any branched-chain paraffins present in the hydrocarbon feed preferably have one or more methyl-branch chains. Paraffinic fractions may be used; preferably any such fraction boils at a temperature not exceeding 100°C. It is particularly preferred to use a fraction having a boiling range of about 15 to about 95°C.

Examples of suitable feedstocks which may be used are straight-run petroleum fractions; the products from the aluminium chloride-catalysed isomerisation of predominantly straight-chain paraffins having 4 to 8 carbon atoms or from other isomerisation processes known in the art; the products obtained by the alkylation of C_2 to C_4 olefins with isoparaffins; or alternatively the product obtained by hydrogenation of the mono-olefins produced by dimerisation of lower olefins such as propylene and isobutene. An example of a commercially available paraffinic hydrocarbon feedstock suitable for the process of the invention is a straight run gasoline fraction from petroleum boiling between about 15 and 95°C.

The molecular oxygen may be fed to the process in the form, for example, of air or mixtures of gas richer or poorer in molecular oxygen than air.

The elevated temperature is preferably in the range from 160 to 200°C. The pressure is chosen such that the reactants are maintained in the liquid phase. Generally pressures in the range 30 to 70 bar will be found suitable.

It is preferred to operate the process in such a manner that substantially all the oxygen fed is absorbed. Thus the concentration of oxygen in the gas leaving the oxidation zone is preferably maintained at not more than 1% wt/wt. The desired rate of absorption may be obtained by adjusting the reaction temperature.

Phosphoric acid may suitably be added in the form of orthophosphoric acid. It may however be added in the form of meta- or pyrophosphoric acid. Group I and Group II metal phosphates may be added in the form of ortho-, meta- or pyrophosphates. The specific phosphorus containing compound is not believed to be critical but it should preferably be soluble in the reaction medium at the concentrations used in order to avoid operational problems. Suitable phosphates include sodium and potassium phosphates. The phosphoric acid and/or phosphate salt may suitably be added in an amount in the range from 0.1 to 1000 ppm, preferably from 0.5 to 100 ppm, calculated as elemental phosphorus.

As hereinbefore mentioned, metals of variable valency, in the form of soluble salts thereof, are known paraffin oxidation catalysts. It has now been found that the increase in selectivity to acetic acid attending the addition of phosphoric acid and/or a phosphate of one or more metals of Groups I and II of the Periodic Table can be further enhanced by the addition of a salt of certain metals of variable valency.

Thus in a further embodiment of the present invention in addition to adding a compound comprising phosphoric acid and/or a phosphate of one or more metals of Groups I and II of the Periodic Table there is also added a compound of a metal of variable valency. Metals of variable valency which may be used include iron, chromium, manganese, cobalt, nickel and molybdenum, of which manganese is preferred. The metal is preferably added in the form of a soluble salt thereof. Examples of suitable soluble salts are the salts of carboxylic acids such as naphthenates, octanoates or acetates. Alternatively inorganic compounds such as the metal salts of carbonic or nitric acid may be employed. Preferably the compound of a metal of variable valency is manganese acetate. When phosphoric acid or a phosphate of one or more metals of Groups I and II is added in addition to a compound of a metal of variable valency the total amount of added compounds may suitably be in the range from 0.1 to 1000, preferably from 0.5 to 100 ppm, calculated as elemental phosphorus plus metal of variable valency.

The process may be operated batchwise or continuously. It is preferred to operate the process continuously and feed the added compound continuously in order to maintain its concentration in the reaction zone within the desired range. The rate at which the added compound is fed during continuous operation will depend on the rate at which the compound is lost from the reaction zone, which in turn will depend upon whether the reaction product is recovered from the reaction zone as a vapour or as a liquid or as a vapour/liquid mixture. The added compound may suitably be fed to the reaction zone in admixture with the paraffinic hydrocarbon feedstock or a C_1 to C_3 aliphatic mono-carboxylic acid or water. The content of the added compound in the reaction zone may be maintained at the desired level by measuring the volume of liquid product withdrawn from the reaction zone and adjusting the amount of the compound fed to the zone to make up for that lost from the zone in the liquid product on the assumption that the content of the compound in the liquid product withdrawn is the same as that in the reaction zone and that none of the compound is deposited therein.

The reaction product may be recovered from the reaction zone and worked up to give individual C_1 to C_3 carboxylic acids in any convenient manner. Thus the reaction product may be recovered from the process as a liquid stream, which may be distilled to remove the low-boiling compound or "light ends" overhead. The residue from this distillation may be subjected to further distillation to recover water and lower carboxylic acids overhead, leaving higher boiling materials as residue. The mixture of water and lower carboxylic acids may then be subjected to further distillation to remove water and to recover formic, acetic and propionic acids and, if desired, butyric acid. Suitable methods of distillation are well-known in the art. The light ends may be recycled directly to the reaction zone. Alternatively, acetone may be recovered from the "light ends" before recycle to the reaction zone.

The invention will now be described with reference to the following Examples and Comparison Tests.

Comparison Test 1

The reaction zone employed was a 5 ft x 4 inch diameter stainless steel cylindrical reactor fitted with an internal draught tube to promote liquid circulation and heated by means of an oil jacket. The paraffinic hydrocarbon feed was a straight-run naphtha with a boiling range of ca 40 to 110°C, containing 27% naphthenes and 6% aromatics, the remainder being paraffins. All feed and recycle streams were fed at the base of the reactor. Air was introduced at the base of the reactor through a sparge ring external to the draught tube. The pressure within the reactor was maintained at 48.3 bar and the temperature at 170 to 174°C to give an oxygen absorption rate of 0.26 kg/l/h.

Liquid products were withdrawn from the base of the reactor through a pressure reducing valve. Organic vapours issuing from the head of the reactor were condensed and returned. Waste gases were vented to atmosphere. The liquid product removed from the base of the reactor was fed to a fractional distillation column. This was a packed glass column operating at atmospheric pressure. The base of the column was maintained at a temperature of 105°C. Low-boiling compounds (ie, materials boiling at temperatures up to 99°C in the presence of water, otherwise known as "light ends") were removed overhead, some being returned to the column as reflux, the rest being returned to the reactor after recovering acetone therefrom. The product from the base of the column was analysed by gas-liquid chromatography to determine the yields of C_1-C_3 acids.

The selectivities on oxygen consumed averaged over four such tests are given in the following Table 1.

This is not an Example according to the invention and is included for the purpose of comparison only.

Example 1

The procedure described in Comparison Test 1 was repeated, except that an aqueous phosphoric acid solution was fed to the reactor at such a rate as to maintain the phosphorus concentration in the liquid product withdrawn from the base of the reactor at 20 ppm. Furthermore, the reaction temperature was allowed to rise to 179°C to keep the oxygen absorption rate constant.

The selectivities on oxygen consumed are given in the following Table 1.

Example 2

The procedure described in Comparison Test 1 was repeated, except that phosphoric acid and manganese acetate in aqueous solution were fed to the reactor at such a rate as to maintain the phosphorus and manganese concentrations in the liquid product withdrawn from the base of the reactor at 10 ppm and 10 ppm respectively. Furthermore, the reaction temperature rose to 184°C.

The selectivities on oxygen consumed are given in the following Table 1.

Example 3

Example 2 was repeated, except that manganese acetate was replaced by nickel acetate.

The selectivities on oxygen consumed are given in the following Table 1.

Example 4

Example 2 was repeated, except that manganese acetate was replaced by cobalt acetate. The reaction temperature fell to 172°C.

The selectivities on oxygen consumed are given in the following Table 1.

All the Examples 1 to 4 demonstrate an improvement in acetic acid selectivity based on oxygen absorbed, the improvement being most marked in Example 2 in which phosphoric acid and manganese acetate were added in combination. Whilst the selectivity to formic acid in Examples 1 to 3 remained substantially unaltered, the selectivity to propionic acid was improved also. The selectivity to formic acid was approximately halved by the addition of cobalt acetate in Example 4 and, whilst the selectivity to acetic acid and propionic acid was increased, this was not so marked as in the case of the addition of phosphoric acid alone (Example 1).

TABLE 1

Oxidation Conditions: Reaction pressure 48.3 bar
Oxygen absorption rate 0.26 kg/1.h
PLE/O_2 ratio* 0.7:1

Example	Comparison Test 1	1	2	3	4
ADDITIVE*	None (4 baseline experiments)	20 ppm P	10 ppm P + 10 ppm Mn	10 ppm P + 10 ppm Ni	10 ppm P + 10 ppm Co
Reaction Temperature °C	170 - 174	179	184	184	172
Selectivities on O_2 Absorbed %w/w					
Formic Acid	10.5 - 11.2	11.3	11.6	11.2	5.5
Acetic Acid	32 - 34	37.7	40.5	38.5	36.3
Propionic Acid	6.2 - 7.0	8.2	7.8	8.4	8.0
Acetone	7.1 - 8.5	8.5	9.0	8.6	8.0

* PLE/O_2 ratio is the weight ratio of "light ends" leaving the reactor to oxygen reacted.

Comparison Test 2

The procedure of Comparison Test 1 was followed except that a better quality naphtha feedstock containing 84% paraffins, 13% naphthenes and 3% aromatics was used. The rate of oxygen absorption, the PLE/O_2 ratio and the operating pressure were the same as used in Comparison Test 1 but the temperature was increased to 181°C.

The selectivities on oxygen absorbed are given in the following Table 2.

This is not an example illustrating the present invention because no phosphoric acid or phosphate was added.

Example 5

The procedure of Comparison Test 2 was repeated except that an aqueous solution of ortho-phosphoric acid was fed to the reactor at such a rate as to maintain the phosphorus concentration in the liquid product withdrawn from the base of the reactor at 2 ppm. Furthermore the reaction temperature was increased to 188°C to maintain the oxygen absorption rate constant.

The selectivities on oxygen absorbed are given in the following Table 2.

Example 6

Example 5 was repeated except that the phosphorus concentration was increased to 10 ppm and the temperature to 194°C.

The selectivities on oxygen absorbed are given in the following Table 2.

Example 7

Example 5 was repeated except that the phosphorus concentration was increased to 20 ppm and the temperature was increased to 193°C.

The selectivities on oxygen absorbed are given in the following Table 2.

TABLE 2

Example	Comparison Test 2	5	6	7
Concentration of phosphoric acid in reactor product (ppm as P)	0	2	10	20
Reaction temperature (°C)	181	188	194	193
Selectivities on O_2 Absorbed, (% w/w)				
Formic Acid	12.2	13.0	12.0	12.0
Acetic Acid	42.0	45.7	47.6	48.9
Propionic Acid	7.6	7.9	8.2	8.7
Acetone	8.9	8.4	9.3	8.8

In all of the Examples 5 to 7 the selectivities to both acetic and propionic acids increased with increasing phosphorus concentration.

Comparison Test 3

The procedure of Comparison Test 2 was followed except that rather more acetone was extracted from the 'light ends' stream before this stream was returned to the oxidation reactor.

The selectivities on oxygen absorbed are given in the following Table 3.

This is not an example of the working of the present invention because no phosphoric acid or phosphate was added.

Example 8

Comparison Test 3 was repeated except that an aqueous solution of ortho-phosphoric acid was fed to the reactor at such a rate as to maintain the phosphorus concentration in the liquid product withdrawn from the base of the reactor at 20 ppm, and the temperature was increased to 193°C to maintain the oxygen absorption rate constant.

The selectivities on oxygen absorbed are given in the following Table 3.

Example 9

Example 8 was repeated except that Na_3PO_4, tri-sodium orthophosphate, was added in place of ortho-phosphoric acid.

The selectivities on oxygen absorbed are given in the following Table 3.

Example 10

Example 8 was repeated except that in place of ortho-phosphoric acid there was added $(NaPO_3)_6$, sodium hexametaphosphate, and the temperature was increased to 194°C.

The selectivities on oxygen absorbed are given in Table 3.

Example 11

Example 8 was repeated except that in place of ortho-phosphoric acid there was added $Na_4P_2O_7$, sodium pyrophosphate, and the temperature was increased to 195°C.

TABLE 3

Example	Comparison Test 3	8	9	10	11
Additive used	None	H_3PO_4	Na_3PO_4	$(NaPO_3)_6$	$Na_4P_2O_7$
Concentration of additive in reactor product (ppm as P)	–	20	20	20	20
Reaction temperature (°C)	181	193	193	194	195
Selectivities on O_2 Absorbed (% w/w)					
Formic Acid	11.8	11.3	10.4	11.1	10.5
Acetic Acid	43.3	43.5	50.5	49.9	50.8
Propionic Acid	7.5	8.2	8.7	8.3	8.5
Acetone	11.0	11.1	11.2	11.9	11.4

In Examples 8 to 11 similar improvements in selectivity to acetic and propionic acids were observed for the different phosphates added.

Example 12

Example 7 was repeated except that the oxygen absorption rate was adjusted to 87% of the value prevailing in the Example and the temperature was increased to 194°C.

The selectivities on oxygen absorbed are given in the following Table 4.

Example 13

Example 12 was repeated except that, in addition to the ortho-phosphoric acid, manganese acetate was added at such a rate as to maintain the manganese concentration in the liquid product withdrawn from the base of the reactor at 10 ppm and the temperature was reduced to 193°C.

The selectivities on oxygen absorbed are given in the following Table 4.

Example 14

Example 13 was repeated except that the ortho-phosphoric acid was added at such a rate as to maintain the phosphorus concentration in the liquid product withdrawn from the base of the reactor at 10 ppm, the manganese acetate feed rate remaining unchanged. The temperature was increased to 194°C.

The selectivities on oxygen absorbed are given in the following Table 4.

Examples 13 and 14 demonstrate the further improvement in selectivity to acetic acid consequent upon the addition of manganese, although the effect is less marked than with the poorer quality naphtha feedstock used in Example 2.

TABLE 4

Example		12	13	14
Additives used				
Phosphoric Acid	(ppm as P)	20	20	10
Manganese Acetate	(ppm as Mn)	-	10	10
Reaction Temperature	(°C)	194	193	194
Selectivities on O_2 Absorbed (% w/w)				
Formic Acid		12.4	12.1	12.3
Acetic Acid		48.8	49.6	49.8
Propionic Acid		8.8	8.6	8.3
Acetone		10.2	10.2	10.1

What we claim is:

1. A process for the production of C_1 to C_3 mono-carboxylic acids, including a substantial proportion of acetic acid, by oxidising in a reaction zone a paraffinic hydrocarbon feedstock with molecular oxygen at a temperature in the range from 150 to 250°C and at an elevated pressure sufficient to maintain the reactants in the liquid phase characterised in that there is added to the reactants a compound comprising phosphoric acid and/or a phosphate of one or more metals of Groups I and II of the Periodic Table.
2. A process according to claim 1 wherein the paraffinic hydrocarbon is a paraffin containing from 4 to 8 carbon atoms in the molecule or a mixture thereof.
3. A process according to either one of the preceding claims wherein the paraffinic hydrocarbon is a paraffinic fraction having a boiling range of about 15 to about 95°C.
4. A process according to claim 3 wherein the paraffinic fraction is a straight run gasoline fraction from petroleum.
5. A process according to any one of the preceding claims wherein the temperature is in the range from 160 to 200°C and the pressure is in the range from 30 to 70 bar.
6. A process according to any one of the preceding claims wherein the Group I or Group II metal phosphate is a phosphate of sodium or potassium.
7. A process according to any one of the preceding claims wherein the phosphoric acid and/or the phosphate salt is added in an amount in the range from 0.1 to 1000 ppm, calculated as elemental phosphorus.

8. A process according to claim 7 wherein the phosphoric acid and/or the phosphate salt is added in an amount in the range 0.5 to 100 ppm, calculated as elemental phosphorus.

9. A process according to any one of the preceding claims wherein, in addition to the phosphoric acid and/or phosphate of one or more metals of Groups I and II, there is also added a compound of a metal of variable valency.

10. A process according to claim 9 wherein the metal of variable valency is iron, chromium, manganese, cobalt, nickel or molybdenum.

11. A process according to claim 10 wherein the metal of variable valency is manganese.

12. A process according to any one of claims 9 to 11 wherein the total amount of added compounds is in the range from 0.5 to 100 ppm, calculated as elemental phosphorus plus metal of variable valency.

13. A process according to any one of the preceding claims when operated in a continuous manner.

14. A process according to any one of the preceding claims wherein the reaction zone is fabricated in stainless steel.

0003399

European Patent Office

EUROPEAN SEARCH REPORT

Application number
EP 79 30 0058

DOCUMENTS CONSIDERED TO BE RELEVANT

Category	Citation of document with indication, where appropriate, of relevant passages	Relevant to claim
D	GB - A - 743 990 (THE DISTILLERS CO.) * Claim 1; page 3, lines 75-80 *	1
X	DE - C - 550 933 (I.G. FARBENINDUSTRIE) * Claim 1; page 1, lines 1-9, 24-25 *	1-1
	GB - A - 879 591 (I.C.I.) * Claims 1,3; page 1, lines 57-60 *	
A	US - A - 3 907 833 (SLINKARD et al.) * Claim 1 *	1
A	US - A - 4 052 417 (SLINKARD et al.) * Claims 1,6,10 *	1

CLASSIFICATION OF THE APPLICATION (Int. Cl.²)

C 07 C 53/02
53/08
53/22
51/20

TECHNICAL FIELDS SEARCHED (Int. Cl.)

C 07 C 53/00
53/02
53/08
53/22
51/20
51/16
51/22
B 01 J 27/16
27/18

CATEGORY OF CITED DOCUMENTS

X: particularly relevant
A: technological background
O: non-written disclosure
P: intermediate document
T: theory or principle underlying the invention
E: conflicting application
D: document cited in the application
L: citation for other reasons

&: member of the same patent family,
corresponding document

☑ The present search report has been drawn up for all claims

Place of search	Date of completion of the search	Examiner
The Hague	12-04-1979	KLAG

EPO Form 1503.1 06.78